

SPACE ELECTROCHEMICAL RESEARCH AND TECHNOLOGY

ABSTRACTS



NASA Lewis Research Center
Cleveland, Ohio

April 9-10, 1991

NASA CP-10067

REFERENCE

**SPACE
ELECTROCHEMICAL
RESEARCH AND
TECHNOLOGY**

ABSTRACTS

NASA

National Aeronautics and
Space Administration

Lewis Research Center
Cleveland, Ohio 44135

April 9-10, 1991

NASA CP-10067

AGENDA
SPACE ELECTROCHEMICAL RESEARCH AND TECHNOLOGY CONFERENCE
NASA LEWIS RESEARCH CENTER
CLEVELAND, OHIO
APRIL 9-10, 1991

Tuesday, April 9, 1991

8:00 a.m. Registration, coffee and doughnuts (Adm. Bldg.)

9:00 a.m. Welcome

J. Stuart Fordyce,
Director, Aerospace Technology Directorate, NASA Lewis
Research Center

9:10 a.m. Henry W. Brandhorst, Jr.,
Chief, Power Technology Division, NASA Lewis Research
Center

Related Overviews

9:20 a.m. Introduction

Marvin Warshay,
Chief, Electro-Chemical Technology Branch, NASA Lewis
Research Center

9:25 a.m. NASA Requirements for Power and Energy Into the 21st Century
Earl Van Landingham, Director, Propulsion, Power and Energy
Division, NASA Headquarters

9:40 a.m. Mission Scenarios and Enabling Power and Storage Technologies for
the Space Exploration Initiative
John C. Mankins, NASA Headquarters

9:55 a.m. The NASA Program for Environmental Control and Life Support
Systems
Peggy L. Evanich, NASA Headquarters

10:10 a.m. Break

Technical Sessions

10:25 a.m. Electrochemistry for Non-Energy Storage Applications
Chairperson

Ernest Yeager, Case Western Reserve University
Co-Chairperson
Richard S. Baldwin, NASA Lewis Research Center

10:30 a.m. Electrolytic Production of Oxygen
Rudolf Keller, EMEC Consultants

10:55 a.m. The Au Cathode in the System $\text{Li}_2\text{CO}_3\text{-CO}_2\text{-CO}$ at 800 to 900 °C
Norman H. Hagedorn, NASA Lewis Research Center

dist. 5-8-91

- 11:20 a.m. SPE[•] Water Electrolyzers in Support of Mission from Planet Earth
J.F. McElroy, Hamilton Standard Division, UTC
- 11:45 a.m. Space Water Electrolysis: Space Station Through Advanced Missions
Ronald J. Davenport, Life Systems, Inc.
- 12:10 p.m. Session Summary
Ernest Yeager, Case Western Reserve University
- 12:20 p.m. Lunch
- 1:30 p.m. The Electrochemical Interface
Chairperson
Supramaniam Srinivasan, Texas A&M University
Co-Chairperson
Patricia L. Loyselle, NASA Lewis Research Center
- 1:35 p.m. The Effects of Platinum on Nickel Electrodes in Nickel Hydrogen Cells
Albert H. Zimmerman, The Aerospace Corporation
- 2:00 p.m. The Nickel(111)/Alkaline Electrolyte Interface
D.A. Scherson, Case Western Reserve University
- 2:25 p.m. Physical and Chemical Analysis of a Ni/H₂ Cell
H. Vaidyanathan, COMSAT Laboratories
- 2:50 p.m. Raman Spectral Observation of a "New Phase" Observed in Nickel Electrodes Cycled to Failure
B.C. Cornilsen, Michigan Technological University
- 3:15 p.m. Break
- 3:30 p.m. Inelastic Neutron Scattering Studies on Nickel Hydroxides From Cycled Ni-Positive Plates of Ni-H₂ Batteries
Juergen Eckert, Los Alamos National Laboratory
- 3:55 p.m. Impedances of Nickel Electrodes Cycled in Various KOH Concentrations
Margaret A. Reid, NASA Lewis Research Center
- 4:20 p.m. High Energy Efficiency and High Power Density Proton Exchange Membrane Fuel Cells - Electrode Kinetics and Mass Transport
Supramaniam Srinivasan, Texas A&M University
- 4:45 p.m. I-BIEM Calculations of the Frequency Dispersion and AC Current Distribution at a Disk/Ring-Disk Electrode
B.D. Cahan, Case Western Reserve University
- 5:10 p.m. Session Summary
Supramaniam Srinivasan, Texas A&M University
- 5:25 p.m. Adjourn

5:30- Social and Dinner
8:00 p.m. (Main Cafeteria)

Wednesday, April 10, 1991

- 8:00 a.m. Registration, coffee and doughnuts
- 8:30 a.m. The Next Generation in Aerospace Batteries and Fuel Cells
Chairperson
Lawrence H. Thaller, The Aerospace Corporation
Co-Chairperson
Patricia M. O'Donnell, NASA Lewis Research Center
- 8:35 a.m. Regenerative Space Fuel Cell Power/Advanced Stack Testing
N.E. Vanderborgh, Los Alamos National Laboratory
- 9:00 a.m. Regenerative Fuel Cell Architectures for Lunar Surface Stationary
and Mobile Power
D.W. Harris, Rocketdyne Division, Rockwell International
- 9:25 a.m. Oxygen Electrodes for Rechargeable Alkaline Fuel Cells - III
L. Swette, Giner, Inc.
- 9:50 a.m. High Performance Oxygen Electrodes for PEM Fuel Cells
V. Jalan, ElectroChem, Inc.
- 10:15 a.m. Break
- 10:30 a.m. Some Recent Studies With the Solid-Ionomer Electrochemical
Capacitor
S. Sarangapani, Giner, Inc.
- 10:55 a.m. PEM Fuel Cells for Passive Operation
O. Adlhart, Ergenics Power Systems, Inc. (EPSI)
- 11:20 a.m. Performance of a Dual Anode Nickel-Hydrogen Cell
Randall F. Gahn, NASA Lewis Research Center
- 11:45 a.m. Multiple Cell Common Pressure Vessel Nickel-Hydrogen Battery
Jeffrey P. Zagrodnik, Johnson Controls, Inc.
- 12:10 p.m. Lunch
- 1:30 p.m. Small Capacity, Low Cost (Ni-H₂) Design Concept for Commercial,
Military, and Higher-Volume Aerospace Applications
William Cook, Eagle-Picher Industries, Inc.
- 1:50 p.m. Mathematical Analyses of the Transport and Reaction Mechanisms in
Solid Oxide Fuel Cells
Thomas M. Maloney, Sverdrup Technology, Inc.
- 2:10 p.m. Sodium Sulfur Cell Technology Flight Experiment
Rebecca R. Chang, Space Systems/Loral

- 2:30 p.m. A Review of Sodium - Metal Chloride Battery Activity at JPL
A.I. Attia, Jet Propulsion Laboratory
- 2:50 p.m. Break
- 3:05 p.m. An AC Impedance Study of the Ni/NiCl₂ Electrode of Sodium/Metal
Chloride Cells
M.C.H. McKubre, SRI International
- 3:25 p.m. Advances in Li-TiS₂ Cell Technology
S. Surampudi, Jet Propulsion Laboratory
- 3:45 p.m. Lithium Polymer Batteries
Boone B. Owens, University of Minnesota
- 4:05 p.m. Session Summary
Lawrence H. Thaller, The Aerospace Corporation
- 4:20 p.m. Closing Remarks
Marvin Warshay, NASA Lewis Research Center
- 4:25 p.m. Adjourn

CONTENTS

Page

ELECTROCHEMISTRY FOR NON-ENERGY STORAGE APPLICATIONS

Chairperson: Ernest Yeager, Case Western Reserve University

Co-Chairperson: Richard S. Baldwin, NASA Lewis Research Center

Electrolytic Production of Oxygen Rudolf Keller, EMEC Consultants	1
The Au Cathode in the System $\text{Li}_2\text{CO}_3\text{-CO}_2\text{-CO}$ at 800 to 900 °C Norman H. Hagedorn, NASA Lewis Research Center	3
SPE [•] Water Electrolyzers in Support of Mission from Planet Earth J.F. McElroy, Hamilton Standard Division, UTC	5
Space Water Electrolysis: Space Station Through Advanced Missions Ronald J. Davenport, Life Systems, Inc.	7

THE ELECTROCHEMICAL INTERFACE

Chairperson: Supramaniam Srinivasan, Texas A&M University

Co-Chairperson: Patricia L. Loyselle, NASA Lewis Research Center

The Effects of Platinum on Nickel Electrodes in Nickel Hydrogen Cells Albert H. Zimmerman, The Aerospace Corporation	9
The Nickel(III)/Alkaline Electrolyte Interface Kuiliong Wang, G.S. Chottiner, and D.A. Scherson, Case Western Reserve University, and Margaret A. Reid, NASA Lewis Research Center	11
Physical and Chemical Analysis of a Ni/H ₂ Cell H. Vaidyanathan, M. Earl, and T. Kirkendall, COMSAT Laboratories . .	13
Raman Spectral Observation of a "New Phase" Observed in Nickel Electrodes Cycled to Failure P.L. Loyselle, X. Shan, and B.C. Cornilsen, Michigan Technological University, and M.A. Reid, NASA Lewis Research Center	15
Inelastic Neutron Scattering Studies on Nickel Hydroxides From Cycled Ni-Positive Plates of Ni-H ₂ Batteries Juergen Eckert and Ravi Varma, Los Alamos National Laboratory, and Lisa Diebolt, Arizona State University	17
Impedances of Nickel Electrodes Cycled in Various KOH Concentrations Margaret A. Reid and Patricia L. Loyselle, NASA Lewis Research Center	19

High Energy Efficiency and High Power Density Proton Exchange Membrane Fuel Cells - Electrode Kinetics and Mass Transport Supramaniam Srinivasan, Omourtag Velev, Arvind Parthasarathy, David J. Manko, and A. John Appleby, Texas A&M University	21
I-BIEM Calculations of the Frequency Dispersion and AC Current Distribution at a Disk/Ring-Disk Electrode B.D. Cahan, Case Western Reserve University	23
THE NEXT GENERATION IN AEROSPACE BATTERIES AND FUEL CELLS	
Chairperson: Lawrence H. Thaller, The Aerospace Corporation	
Co-Chairperson: Patricia M. O'Donnell, NASA Lewis Research Center	
Regenerative Space Fuel Cell Power/Advanced Stack Testing N.E. Vanderborgh, J.C. Hedstrom, and J.R. Huff, Los Alamos National Laboratory	25
Regenerative Fuel Cell Architectures for Lunar Surface Stationary and Mobile Power D.W. Harris, S.P. Gill, T.M. Nguyen, and J.J. Vrolyk, Rocketdyne Division, Rockwell International	27
Oxygen Electrodes for Rechargeable Alkaline Fuel Cells - III L. Swette and N. Kackley, Giner, Inc.	29
High Performance Oxygen Electrodes for PEM Fuel Cells V. Jalan, M. Desai, and B. Morrisaeu, ElectroChem, Inc.	31
Some Recent Studies With the Solid-Ionomer Electrochemical Capacitor S. Sarangapani, J. Forchione, A. Griffith, and A. LaConti, Giner, Inc., and R. Baldwin, NASA Lewis Research Center	33
PEM Fuel Cells for Passive Operation O. Adlhart, Ergenics Power Systems, Inc. (EPSI)	35
Performance of a Dual Anode Nickel-Hydrogen Cell Randall F. Gahn, NASA Lewis Research Center	37
Multiple Cell Common Pressure Vessel Nickel-Hydrogen Battery Jeffrey P. Zagrodnik and Michael D. Eskra, Johnson Controls, Inc.	39
Small Capacity, Low Cost (Ni-H ₂) Design Concept for Commercial, Military, and Higher-Volume Aerospace Applications William Cook, Ron Smith, and James Wheeler, Eagle-Picher Industries, Inc.	41
Mathematical Analyses of the Transport and Reaction Mechanisms in Solid Oxide Fuel Cells Thomas M. Maloney, Sverdrup Technology, Inc., Lewis Research Center Group, and Dennis W. Dees, Argonne National Laboratory	43
Sodium Sulfur Cell Technology Flight Experiment Rebecca R. Chang, Space Systems/Loral	45

A Review of Sodium - Metal Chloride Battery Activity At JPL B.V. Ratnakumar, A.I. Attia, and G. Halpert, Jet Propulsion Laboratory	47
An AC Impedance Study of the Ni/NiCl ₂ Electrode of Sodium/Metal Chloride Cells B.J. Dougherty, M.C.H. McKubre, S.I. Smedley, and F. Tanzella, SRI International	49
Advances In Li-TiS ₂ Cell Technology S. Surampudi, D.H. Shen, C.-K. Huang, F. Deligiannis, A.I. Attia, and G. Halpert, Jet Propulsion Laboratory	51
Lithium Polymer Batteries Boone B. Owens, University of Minnesota	53

NOTES

ELECTROLYTIC PRODUCTION OF OXYGEN

Rudolf Keller
EMEC Consultants
Export, Pennsylvania 15632

Oxygen is a valuable commodity in space, for life support and - even more so - as propellant. Substantial savings have been projected for future missions if oxygen could be produced on the Moon from local resources.

Some of the most promising approaches to extract oxygen from lunar resources involve electrochemical oxygen generation. In a straightforward concept called "magma electrolysis," suitable oxides (silicates), as they are readily found on the lunar surface, are molten at 1300-1500 °C and the melt electrolyzed. Residual melt can be discarded after partial electrolysis. Alternatively, lunar soil may be dissolved in a molten salt and electrolyzed. In this approach, temperatures are lower and melt conductivities higher, but oxides of the process feed need to be fully electrolyzed or otherwise eliminated from the process system to retain proper characteristics of the electrolyte. Both possibilities are being studied in the laboratory, the development of a suitable anode being a critical element of present efforts.

The reduction of ilmenite by hydrogen, to generate water from which the oxygen can be extracted, has also been studied experimentally (Carbothek Process). Thermodynamically, an attractive energy consumption can be projected for this approach. Electrolysis of the water at elevated temperature is being considered.

Although know-how from terrestrial technology can be applied, many unique problems that require innovative solutions arise in the development of such an unconventional process. Time and effort needed for successful development should not be underestimated.

NOTES

THE Au CATHODE IN THE SYSTEM $\text{Li}_2\text{CO}_3\text{-CO}_2\text{-CO}$ AT 800 TO 900 °C

Norman H. Hagedorn
NASA Lewis Research Center
Cleveland, Ohio 44135

Gold is one of several metals being evaluated at NASA Lewis Research Center as positive electrode catalysts for an alkali metal/molten alkali metal carbonate/carbon dioxide electrochemical cell. Such a cell is proposed for CO_2 -rich planetary atmospheres such as those of Mars and Venus. Its application could be as a primary power supply, as a secondary power supply recharged either "chemically" by replenishment of the alkali metal or electrochemically from a central station power source, or as a converter of carbon dioxide to oxygen via a complete electrochemical cycle. For the work being reported, lithium was assumed to be the alkali metal of choice for the negative electrode of the cell, and therefore molten lithium carbonate was the electrolyte used in the Au electrode experiments.

Cathodic linear sweep voltammetry (LSV) was the primary analytical technique for evaluating the performance of the Au cathode. The state variables of interest comprised the cell temperature and the total pressure and composition of the reactant gas. In the absence of operational difficulties, the effect of bubbling the reactant gas through the melt was also determined. On the basis of the variation of electrode performance with changes in these parameters, inferences have been made concerning the electrochemical and chemical processes at and near the electrode. The results of post-test micrographic analyses of the Au cathode are also presented. An attempt is then made to project from the experimental results to some relevant conclusions pertaining to a gold cathode in a practical alkali metal - carbon dioxide cell.

NOTES

***SPE[®] WATER ELECTROLYZERS IN SUPPORT OF MISSION FROM PLANET EARTH**

J.F. McElroy
Hamilton Standard Division, UTC
Windsor Locks, Connecticut 06906

During the 1970's the SPE Water Electrolyzer, which uses ion exchange membranes as its sole electrolyte, was developed for nuclear submarine metabolic oxygen production. These developments included SPE water electrolyzer operation at up to 3000 psia and at current densities in excess of 1000 amps per square foot. SPE water electrolyzer systems are now fully qualified for both U.S. and U.K. Navies with tens of thousands of system hours accumulated at sea. An overview of these programs will be provided.

During the 1980's the basic SPE water electrolyzer cell structure developed for the Navies was incorporated into several demonstrators for NASA's Space Station Program. Among these were

- SPE regenerative fuel cell for electrical energy storage
- SPE water electrolyzer for metabolic oxygen production
- High Pressure SPE water electrolyzer for reboost propulsion reactant production

Details of construction and performance of these demonstrators will be provided.

In the 1990's the emphasis will be the development of SPE electrolyzers for Mission from Planet Earth. Currently identified potential applications for the SPE water electrolyzer include

- SPE water electrolyzers operating at high pressure as part of a regenerative fuel cell extraterrestrial surface energy storage system
- SPE water electrolyzers for propulsion reactants production from extraterrestrial indigenous materials
- SPE water electrolyzers for metabolic oxygen and potable water production from reclaimed water

Extraterrestrial Surface Energy Storage

Recent studies have shown, that short of nuclear power, solar energy combined with an oxygen-hydrogen regenerative fuel cell is a mission enabling technology for lunar and Mars bases. The long occult periods, 14 days and 12 hours respectively, make the separation of power and energy in the oxygen-hydrogen regenerative fuel cell decisive. The SPE water electrolyzer in particular has demonstrated the life, stability, reliability, and high pressure capability required for an extraterrestrial surface energy storage system. Preliminary system characteristics will be discussed.

*SPE[®] is a registered trademark of the Hamilton Standard Division of United Technologies Corporation.

Propulsion Reactant Production

The use of the SPE water electrolyzer to produce high pressure oxygen and hydrogen from available water has been demonstrated. However, the availability of sufficient water for this purpose on extraterrestrial surfaces is in considerable doubt. At least on the martian surface there is no doubt in the availability of carbon dioxide. A system which combines the SPE water electrolyzer with a Sabatier and a carbon formation reactor can produce methane and oxygen from this carbon dioxide and hydrogen delivered from Earth. This arrangement can increase the Earth return propulsive reactant mass leverage by up to 18 fold. Each of the required subsystems has been demonstrated individually with high confidence that they can be combined to produce the desired results. A top level schematic and subsystem reactions will be provided along with equipment mass estimates for two potential Mars return missions.

Metabolic Oxygen - Potable Water Production

The generation of metabolic oxygen from processed hygiene water in the SPE water electrolyzer has been recently demonstrated. Tests conducted on the quality of the water at various points in the system indicated that organic species were being oxidized within the oxygen chamber and that the proton pumped water was free of any detectable organics. These observations have led to the speculation that the SPE water electrolyzer can be configured to produce potable water as well as metabolic oxygen. For manned lunar and Mars bases and the lunar and Mars manned transportation vehicles, a combined oxygen generator and potable water processor could have significant mass advantages. A system schematic and water analyses will be discussed.

SPACE WATER ELECTROLYSIS: SPACE STATION THROUGH ADVANCED MISSIONS

Ronald J. Davenport and Franz H. Schubert
Life Systems, Inc.
Cleveland, Ohio 44122

Static Feed Electrolysis technology has long been recognized as being important in meeting the National Aeronautics and Space Administration's requirements for life support within the Space Station Freedom Program and future, advanced missions. The Static Feed Electrolysis technology makes it possible to very efficiently generate oxygen to sustain the crew, and hydrogen for the efficient and economical operation of other space systems.

More recently, additional applications for the Static Feed Electrolysis technology have been evaluated and tested. This paper summarizes the results of those studies. The applications addressed here are those involving energy storage, propulsion, extravehicular activity, and other specialized applications, such as providing support for experimentation and manufacturing. The Environmental Control and Life Support System application is included for comparison.

NOTES

THE EFFECTS OF PLATINUM ON NICKEL ELECTRODES IN NICKEL HYDROGEN CELLS

Albert H. Zimmerman
The Aerospace Corporation
El Segundo, California 90245

The hydrogen electrode in the NiH_2 cells consists of a platinum catalyst that is in contact with the cell electrolyte. Typically this platinum catalyst electrode is at a reducing potential where the platinum is thermodynamically stable in the metallic state. However, conditions can arise in the nickel hydrogen cell where the voltage of the platinum catalyst electrode rises to the highly oxidizing potential of the nickel electrode, whereupon the Pt metal is unstable relative to platinum oxide. Since platinum oxide has some solubility in alkaline electrolyte, dissolved platinum species can conceivably migrate to, and interact with, the nickel electrode.

This condition has been observed in several nickel hydrogen cells from the Hubble Space Telescope and from military programs. It must be pointed out that in these cases, cell performance was improved relative to cells that did not display this condition. In each case, the platinum seemed to have reacted with the nickel electrode during cell storage. Typically, in these cells there was an indication of a nickel precharge condition as well. This is not fully unexpected, since with a nickel precharge, cell storage at low cell voltages will drive the platinum catalyst electrode to the nickel electrode voltage. Chemical analysis of nickel electrodes from these cells indicated significant amounts of a platinum containing oxide that also seemed to be associated with large amounts of nickel and cobalt. Electrochemical Voltage Spectroscopic (EVS) analysis of these nickel electrodes revealed an anomalous material having a reduction potential of 0.16 volts (vs. Hg/HgO in 31% KOH).

The same anomalous material was produced in nickel electrodes in laboratory cells by placing partially discharged nickel electrodes in contact with KOH electrolyte that was also in intimate contact with Pt black or a Pt catalyst electrode. The formation of this anomalous material was found to not depend on electrolyte concentration or temperature significantly, but was quite sensitive to the charge state and the amount of cobalt in the nickel electrode. In fact, cobalt was required if this material was to be formed. Examination of redox potentials and thermal stability of the material indicated that it was likely to be $\text{Ni}_{0.5}\text{Co}_{0.5}\text{OOH}$. This nickel-cobalt oxyhydroxide is likely to form by catalytic interaction of platinate ions with the normal nickel electrode active material which remains charged when a cell has nickel precharge. Data obtained so far indicate that this material improves nickel electrode performance by maintaining an electronically conductive matrix through the active material as it discharges. It remains to be established whether this effect improves or degrades cycle life, and how this material (and cell performance) will respond to loss of nickel precharge because of sinter corrosion later in life.

NOTES

THE NICKEL(111)/ALKALINE ELECTROLYTE INTERFACE

Kuilong Wang, G.S. Chottiner, and D.A. Scherson
Case Western Reserve University
Cleveland, Ohio 44106

and

Margaret A. Reid
NASA Lewis Research Center
Cleveland, Ohio 44135

The electrochemical properties of Ni(111) prepared and characterized in ultra high vacuum, UHV, by surface analytical techniques have been examined in alkaline media by cyclic voltammetry using an UHV-electrochemical cell transfer system designed and built in this laboratory. Prior to the transfer, the Ni(111) surfaces were exposed to saturation coverages of CO in UHV in an attempt to protect the surface from possible contamination with other gases during the transfer.

Temperature Programmed Desorption, TPD, of CO-dosed Ni(111) surfaces displaying sharp $c(4 \times 2)$ LEED patterns, subsequently exposed to water-saturated Ar at atmospheric pressure in an auxiliary UHV compatible chamber and finally transferred back to the main UHV chamber, yielded CO_2 and water as the only detectable products. This indicates that the CO-dosed surfaces react with water and/or bicarbonate and hydroxide as the most likely products. Based on the integration of the TPD peaks, the combined amounts of H_2O and CO_2 were found to be on the order of a single monolayer.

The reacted $c(4 \times 2)\text{CO}/\text{Ni}(111)$ layer seems to protect the surface from undergoing spontaneous oxidation in strongly alkaline solutions. This was evidenced by the fact that the open circuit potential observed immediately after contact with deaerated 0.1 M KOH was about 0.38 V vs. DHE, drifting slightly towards more negative values prior to initiating the voltammetric scans. The average ratio of the integrated charge obtained in the first positive linear scan in the range of 0.35 to 1.5 V vs. DHE (initiated at the open circuit potential) and the first (and subsequent) linear negative scans in the same solution yielded for various independent runs a value of 3.5 ± 0.3 .

Coulometric analysis of the cyclic voltammetry curves indicate that the electrochemically formed oxyhydroxide layer involves a charge equivalent to 3.2 ± 0.4 layers of Ni metal.

NOTES

PHYSICAL AND CHEMICAL ANALYSIS OF A Ni/H₂ CELL

H. Vaidyanathan, M. Earl, and T. Kirkendall
COMSAT Laboratories
Clarksburg, Maryland 20871

A cycled nickel-hydrogen (Ni/H₂) cell was subjected to destructive physical analysis to determine the reason for a capacity loss after 5,967 cycles at 60-percent depth of discharge. The positive plates in the cell were analyzed in terms of chemical composition, active material utilization, charge efficiency, and thickness increase. The microstructure of a cross section of the positive plate was determined by back-scattered electron image analysis.

There were no indications of a soft short, which is consistent with the measured charge retention of 79 percent in 72 hours of charge stand. However, the electrode stack displayed evidence of rapid oxygen reaction with hydrogen. Numerous cracks were seen in the Gore-Tex backing, as well as burn holes in the negative electrode and burn marks and melting in the gas distribution screen. The charge efficiency of the positive plate in flooded KOH was 84 to 90 percent at 50-percent state-of-charge condition, whereas an uncycled electrode has an efficiency of 100 percent at the same state of charge. The active material utilization of the plate during flooded KOH capacity discharge was 82 percent, which is also low. The positive plate thickness increase was 10.5 percent.

The results of the study suggest that the capacity loss in the cell is traceable to low charge acceptance and low active material utilization at the positive plate. Microstructural analysis has given preliminary indications that a new phase of active material is formed with cycling.

NOTES

RAMAN SPECTRAL OBSERVATION OF A "NEW PHASE" OBSERVED IN NICKEL ELECTRODES CYCLED TO FAILURE

P.L. Loyselle,* X. Shan, and B.C. Cornilsen**
Michigan Technological University
Houghton, Michigan 49931

and

M.A. Reid
NASA Lewis Research Center
Cleveland, Ohio 44135

A "new phase" is reported in nickel electrodes from Ni/H₂ boilerplate cells which were cycled to failure in electrolyte of variable KOH concentration. These electrodes originated from cells tested at the Hughes Aircraft Company (ref. 1). Raman spectra clearly show the presence of this phase, and these spectra have been used to quantify the amounts present in these electrodes (in the volume sampled by the laser beam). Raman spectroscopy has been found to be capable of differentiating the various phases which can be present in nickel electrodes (ref. 2). This differentiation is possible because of the structural variation observed for these phases. Ten of twelve electrodes examined contain at least some of this new phase. The presence of this "new phase" correlates with cell failure, and it is proposed that the presence of this phase may play a role in early electrode failure.

References

1. H.S. Lim and S.A. Verzwylt, "KOH Concentration Effect on the Cycle Life of Nickel-Hydrogen Cells IV. Results of Failure Analyses, J. Power Sources, 29 503-519 (1990).
2. B.C. Cornilsen, X., Shan, and P.L. Loyselle, "Structural Comparison of Nickel Electrodes and Precursor Phases," J. Power Sources, 29 453-466 (1990).

Support by NASA Lewis Research Center under Grant No. NAG3-519 is gratefully acknowledged.

*Current address: NASA Lewis Research Center.

**Author to whom correspondence should be addressed.

NOTES

INELASTIC NEUTRON SCATTERING STUDIES ON NICKEL HYDROXIDES
FROM CYCLED Ni-POSITIVE PLATES OF Ni-H₂ BATTERIES

Juergen Eckert and Ravi Varma
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

and

Lisa Diebolt
Arizona State University
Tempe, Arizona 85287

We have carried out inelastic neutron scattering (INS) studies on several samples of nickel hydroxide from cycled battery plate materials as well as β -Ni(OH)₂ in an effort to determine the form and importance of excess protons in the lattice on the battery activity. Apart from several vibrational bands identifiable with varying relative amounts of α - and β -phase Ni(OH)₂, additional features can be identified in the spectra whose intensities correlate strongly with the cycling history of the materials. We will describe the possible origin of these bands and attendant implications for battery cycleability.

NOTES

IMPEDANCES OF NICKEL ELECTRODES CYCLED IN VARIOUS KOH CONCENTRATIONS

Margaret A. Reid and Patricia L. Loyselle
NASA Lewis Research Center
Cleveland, Ohio 44135

Impedances were measured of electrodes from boiler-plate cells that had been cycled in KOH concentrations from 21% to 36 %. These cells had been cycled under accelerated conditions at 80% DOD to failure, defined as low end of discharge voltage. Cell life ranged from about 1,000 to 40,000 cycles. The impedances were measured at five voltages corresponding to low states of charge. The results were analyzed using a standard circuit model including a Warburg impedance term. The kinetic resistances and Warburg slopes were greater for those electrodes which had failed earliest. Other circuit models have also been examined. The results are considered indicative but not conclusive, since the cells had been stored after failure for varying lengths of time which is known to affect the impedance. In order to minimize the effects of storage, the electrodes were cycled 10 times before the impedance measurements were taken.

NOTES

HIGH ENERGY EFFICIENCY AND HIGH POWER DENSITY PROTON EXCHANGE MEMBRANE FUEL CELLS - ELECTRODE KINETICS AND MASS TRANSPORT

Supramaniam Srinivasan, Omourtag Velev, Arvind Parthasarathy,
David J. Manko, and A. John Appleby
Texas A&M University
College Station, Texas 77843-3577

High energy efficiency and high power density fuel cells are vitally needed for space and terrestrial, particularly transportation, applications. Of the essential criteria for the attainment of high energy efficiencies and high power densities are (1) low activation overpotentials - the major contributor to activation overpotential is the oxygen reduction reaction which has an exchange current density of at least three orders of magnitude less than that of hydrogen oxidation; (2) minimal mass transport overpotential - the structure of the state-of-the-art fuel cell electrodes is such that there is minimal mass transport up to high current density in low to medium temperature acid and alkaline electrolyte fuel cells; and (3) negligible ohmic overpotential, the main cause of which is the resistance of the electrolyte. Of all types of fuel cells (i.e., with acid, alkaline, molten carbonate, solid oxide, and solid polymer electrolytes), only the alkaline and solid polymer electrolyte fuel cells have demonstrated high energy efficiencies and high power densities. The alkaline hydrogen/oxygen fuel cell systems have been and are being successfully used to provide auxiliary power in space vehicles (Apollo, Space Shuttle). However, the solid polymer electrolyte fuel cell, which demonstrated the first major application of fuel cells (i.e., in the Gemini flights), appears most attractive as a power source for long range space missions (Space Station, and lunar and Mars Missions) as well as terrestrial transportation application. The main reasons for the "come back" of the solid polymer electrolyte (more recently renamed the proton exchange membrane) fuel cell are (1) the discovery of highly stable perfluorinated sulfonic acid ionomers with high ionic conductivities, (2) the high performance of oxygen electrode kinetics at the Pt/proton exchange membrane interface, and (3) its CO_2 rejecting capability. This paper presents (1) the methods used to attain high energy efficiencies and high power densities in proton exchange membrane fuel cells with high and low platinum loading electrodes; (2) a novel micro-electrode method using pseudo-steady state, chronoamperometric, and AC impedance techniques to determine (i) the electrode kinetic parameters for oxygen reduction at the Pt/proton exchange membrane interface, and (ii) the solubilities and diffusion coefficients of oxygen in the membrane; (3) evidence for the lack of net water transport from anode to cathode during fuel cell operation; and (4) modeling and experimental analyses of the cell potential vs. current density plots in a proton exchange membrane fuel cell, which reveals the needed research and development to further increase energy efficiencies and power densities.

NOTES

I-BIEM CALCULATIONS OF THE FREQUENCY DISPERSION AND AC CURRENT DISTRIBUTION AT A DISK/RING-DISK ELECTRODE

B.D. Cahan
Case Western Reserve University
Cleveland, Ohio 44106

The Iterative Boundary Equation Method (I-BIEM) has been applied to the problem of frequency dispersion at a disk electrode in a finite geometry. The I-BIEM permits the direct evaluation of the AC potential (a complex variable) using complex boundary conditions. The point spacing was made highly non-uniform, to give extremely high resolution in those regions where the variables change most rapidly (i.e., in the vicinity of the edge of the disk). Results are analyzed with respect to "IR correction," equipotential surfaces, and reference electrode placement. The current distribution is also examined for a ring-disk configuration, with the ring and the disk at the same AC potential. It is shown that the apparent impedance of the disk is inductive at higher frequencies. The results are compared to analytic calculations from the literature, and usually agree to better than 0.001%.

NOTES

REGENERATIVE SPACE FUEL CELL POWER/ADVANCED STACK TESTING

N.E. Vanderborgh, J.C. Hedstrom, and J.R. Huff
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

The objective of the surface power program is to develop Solar-based Power Technology to a level of readiness sufficient to enable or enhance extra-terrestrial surface missions to the Moon or Mars. Technology will be developed in the areas of solar power generation, energy storage, and electrical power management, aimed at meeting general requirements of a system capable of delivering 25 kWe of user power for 20,000 hours in an autonomous operating mode. Advancing the technologies for energy storage and power generation and coupling their performance potentials with an advanced, low-mass, reliable electrical power-management system can lead to surface-power systems with high system specific power for lunar and martian applications.

Regenerative fuel cells (RFC) provide power generation and storage capabilities. A technology assessment and tradeoff study had evaluated contemporary electrochemical technologies for the following RFC system characteristics: 25 kWe continuous, stand-alone operation, lunar and martian surface compatibility, 65% system turnaround efficiency, 500 Wh/kg martian surface, and 800 Wh/kg lunar surface. PEM and alkaline technologies have both been evaluated. This study identified lifetime and reliability of both component and system as concerns. Operational RFC systems must include compact reactant storage. The study results show that, due to the long lunar night, reactant storage considerations dominate the mass and volume budgets. Minimum mass systems utilize highly efficient fuel cells, operating at a voltage of >0.9 V/cell. Inefficiencies in electrolysis hardware are compensated by larger primary power components. Thermal management of RFC systems with liquid water requires novel RFC system designs.

Studies are also underway to evaluate PEM fuel cell stack hardware under high efficiency, long term operation. Graphite hardware supplied by Ballard Power Systems is under test. Fuel cell stack hardware with ion exchange membranes supplied by the Du Pont Company (Nafion[®]) and Dow Chemical Company (Dow experimental membrane) are evaluated using hydrogen and oxygen gas feeds. Tests to date show the importance of thermal and water management, including water quality, for obtaining long term, highly efficient operation. Maximum operating time obtained thus far at the 4 kW stack level is 780 hours with the Nafion[®] membrane.

NOTES

REGENERATIVE FUEL CELL ARCHITECTURES FOR LUNAR SURFACE STATIONARY AND MOBILE POWER

D.W. Harris, S.P. Gill, T.M. Nguyen, and J.J. Vrolyk
Rocketdyne Division, Rockwell International
Canoga Park, California 91300

Power needs projected for the lunar and Mars exploration missions range from a few kilowatts for initial manned outposts and rovers to hundreds of kilowatts for permanent bases and in situ resource utilization. The 354 hour lunar night presents a formidable challenge in energy storage systems for non-nuclear power systems. The photovoltaic/Regenerative Fuel Cell (PV/RFC) is currently being considered as an option to meet the initial low power requirements.

For lunar applications, the RFC mass can be a critical drive in the overall PV/RFC system mass. For the long duration nighttime operation missions, the hydrogen/oxygen (H_2/O_2) reactants and storage are the dominant components from a mass standpoint. It is important, therefore, to examine options which may reduce the reactant and storage mass and, thereby, result in mass savings for the overall PV/RFC system.

Various RFC configurations for both the stationary and the mobile lunar missions have been examined using Rocketdyne's RFC computer model. For the stationary applications, A GaAs/Ge PV array with a 3000-psi gas storage proton exchange membrane (PEM) RFC providing 25 kWe during the day and 12.5 kWe at night was designed. PV/RFC systems utilizing supercritical H_2/O_2 storage and cryogenic H_2/O_2 storage for the RFCs were then compared with the baseline high pressure gas storage RFC system. Preliminary results indicate that for long duration nighttime operation missions, the supercritical H_2/O_2 storage RFC systems offer over 20% mass advantage over the high pressure gas storage, while the mass savings for the cryogenic H_2/O_2 storage RFC systems can be as high as 50%.

For mobile missions, a 2.5 kWe RFC system was designed and characterized. Two different options were examined for this short duration operation (8 hours) system. One option was the RFC configuration on the vehicle operating for 8 hours and then returning to a central station for electrical recharge. The other was a primary fuel cell (PFC) system which was recharged with H_2/O_2 reactants.

For higher power level mobile missions, RFC concepts utilizing larger and/or multiple cell stacks were evaluated. The individual cell area was kept constant. This technique resulted in realizing an economy of scale for higher power RFCs while avoiding new development costs associated with cells of different size.

NOTES

OXYGEN ELECTRODES FOR RECHARGEABLE ALKALINE FUEL CELLS - III

L. Swette and N. Kackley
Giner, Inc.

Waltham, Massachusetts 02254-9147

The primary objective of this program is the investigation and development of electrocatalysts and supports for the positive electrode of moderate-temperature single-unit rechargeable alkaline fuel cells. Viable candidate materials must meet the following requirements: (1) good electrical conductivity (a more demanding requirement for supports than for electrocatalysts), (2) high resistance to chemical corrosion and electrochemical oxidation and/or reduction, and (3) electrocatalysts, in addition, must exhibit high bifunctional electrocatalytic activity (O_2 evolution and reduction). Advanced development will require that the materials be prepared in high-surface-area forms, and may also entail integration of various candidate materials (e.g., one or two electrocatalysts distributed on a less active support material).

The phase purity, BET surface area, and electrical conductivity are determined for all candidate supports and catalysts. Candidate materials of acceptable conductivity ($>1 \text{ ohm-cm}^{-1}$) are subjected to both chemical and electrochemical corrosion testing. Potential support materials identified are $LaNiO_3$, Li_xNiO_y , ZrN , $PbPdO_2$. Deposition of a catalyst onto any of these materials will require advanced development.

To evaluate the bifunctional oxygen activity of candidate catalysts, Teflon-bonded electrodes are fabricated and tested in a floating electrode configuration. For preliminary testing, catalysts of interest should show $<500 \text{ mV}$ polarization (from 1.2 V) in either mode at 200 mA/cm^2 . In advanced development, our goal is to reduce the polarization to about $300\text{--}350 \text{ mV}$. Potential catalysts identified as candidates for the positive electrode (not necessarily bifunctional) are $Na_xPt_3O_4$, IrO_2 , RhO_2 , Rh , Pt , $NiIrO_3$, and $CoIrO_3$.

To date only one material, $Na_xPt_3O_4$, has shown promising bifunctional catalytic activity. Recent work has emphasized electrode physical structure development. We have found that a bifunctional performance can be improved by integrating dual structures, i.e., a balanced uniform blend of two catalyst/TFE agglomerates, one optimized for O_2 evolution, one optimized for O_2 reduction. This approach allows a choice of a single bifunctional catalyst for both structures ($Na_xPt_3O_4$), or two monofunctional catalysts (e.g., Pt for O_2 reduction: IrO_2 for O_2 evolution). Integration of these yields an electrode that has superior bifunctional performance than either structure by itself.

NOTES

HIGH PERFORMANCE OXYGEN ELECTRODES FOR PEM FUEL CELLS

V. Jalan, M. Desai, and B. Morrisaeu
ElectroChem, Inc.
Woburn, Massachusetts 01801

The objective of this research is to attain the highest level of performance in proton exchange membrane (PEM) based fuel cells for aerospace applications. Platinum black electrodes with a loading of 10 mg Pt/cm² on three different backing materials were fabricated by ElectroChem and evaluated in single cells under a variety of operating conditions. Using hydrogen and oxygen pressurized to 5 atm, a current density of 2000 mA/cm² was achieved at a cell potential of 0.7 V and a cell temperature of 95 °C. This is significantly higher than the best performance reported for this type of fuel cell under any operating conditions. Optimization of the electrode structure and the nature of the electrode/membrane interface are particularly crucial to the achievement of high power density, as is the use of an improved membrane, like those being produced experimentally by Du Pont and Dow Chemical Company. Other important factors include the operating pressure, cell temperature, control of reactant gas humidification, and gaskets/seals. This work demonstrates that the power density of PEM fuel cells may be improved by increasing platinum loading while maintaining a high degree of platinum utilization. The implication for space power is a substantial reduction in both mass and volume for a power plant of the same capacity.

NOTES

SOME RECENT STUDIES WITH THE SOLID-IONOMER ELECTROCHEMICAL CAPACITOR

**S. Sarangapani, J. Forchione, A. Griffith, and A. LaConti
Giner, Inc.**

Waltham, Massachusetts 02254-9147

and

**R. Baldwin
NASA Lewis Research Center
Cleveland, Ohio 44135**

Giner, Inc., has developed a high-energy-density, all-solid-ionomer electrochemical capacitor, completely free of liquid electrolyte. The novel features of this device include (1) a three-dimensional metal oxide-particulate-ionomer composite electrode structure and (2) a unitized repeating cell element. The composite electrode structures are bonded to opposite sides of a thin sheet of a solid proton-conducting ionomer membrane and form an integrally bonded membrane and electrode assembly (MEA). Individual MEAs can be stacked in series as bipolar elements to form a multiple cell device. The discharge characteristics and energy storage properties of these devices are described. Typical capacitance measured for a unit cell is 1 F/cm^2 . Life testing of a multicell capacitor on an intermittent basis has shown that, over a 10,000-hour period, the capacitance and resistance of the cell has remained invariant. There has been no maintenance required on the device since it was fabricated. Other multicell units of shorter life duration have exhibited similar reliable performance characteristics.

Recent work has focused on increasing the capacitance of the unitized structure and improving the low-temperature characteristics. The approaches and experimental results will be presented.

Some possible advanced NASA applications for these unique all-solid-ionomer devices will be discussed.

NOTES

PEM FUEL CELLS FOR PASSIVE OPERATION

O. Adlhart
Ergenics Power Systems, Inc. (EPSI)
Ringwood, New Jersey 07456

High thermal efficiency and operational reliability are crucial elements for the applicability of PEM fuel cells for aerospace requirements. Passive systems operating at moderate current densities are needed for these missions. EPSI has developed a passive H_2/O_2 PEM cell technology. It relies on dead end reactant supply, internal reactant prehumidification, and waste heat dissipation by radiation or conduction to a cooling loop. A unique feature of the EPSI technology is the use of pressure enhanced wicking for product water removal. This process utilizes the mobility of product water in hydrophilic, porous collector structures, its transport in suitable wicking manifolds, and its eventual rejection from the stack in a gas/water separation unit as liquid water. The porous structures of the cell stack are separated by nonporous metallic gas separation members. They assure high shock and vibration tolerance. Devices with up to 1 kW rating have been developed. Specifically, a 200 watt, 28 volt system is under advanced development for the Space Station EMU (Extravehicular Mobility Unit). In this case, since volume is important, the PEM cell is integrated with a hydride hydrogen storage subsystem. The paper describes design and performance features of EPSI PEM fuel cell hardware.

NOTES

PERFORMANCE OF A DUAL ANODE NICKEL-HYDROGEN CELL

Randall F. Gahn
NASA Lewis Research Center
Cleveland, Ohio 44135

Nickel-hydrogen batteries are presently being used for energy storage on satellites in low Earth orbit and in geosynchronous orbit, and have also been selected for use on the proposed Space Station Freedom. Development continues on the cell technology in order to improve the specific energy and lengthen the cycle life.

An experimental study was conducted to compare the voltage performance of a nickel-hydrogen cell containing a dual anode with the standard cell design which uses a single hydrogen electrode. Since the principle voltage loss in a nickel-hydrogen cell is attributed to the mass transport and resistive polarization parameters of the nickel electrode, addition of a hydrogen electrode on the other side of the nickel electrode should reduce the electrochemical polarizations by a factor of two.

A 3.5 in. diameter boilerplate cell with a single 30 mils thick nickel electrode was cycled under various current conditions to evaluate its performance with a single anode and then with a double anode. A layered separator consisting of one Zircar cloth separator and one radiation-grafted polyethylene separator were used between the electrodes. The electrolyte was 26% KOH, and the tests were done at room temperature. The discharge voltage characteristics were determined as a function of current and depth-of-discharge. At the 4C discharge rate and 50% DOD, the voltage of the dual anode cell was 100 mV higher than the single anode cell. At 75% DOD the dual anode cell voltage was about 130 mV higher than the standard cell design. Resistances of the two cell designs obtained from the slope of the mid-discharge voltages plotted against various currents indicated that the dual anode cell resistance was one-half of the state-of-the-art cell.

NOTES

MULTIPLE CELL COMMON PRESSURE VESSEL NICKEL-HYDROGEN BATTERY

Jeffrey P. Zagrodnik and Michael D. Eskra
Johnson Controls, Inc.
Milwaukee, Wisconsin 53212

Johnson Controls, Inc., has developed a multiple cell CPV Nickel Hydrogen battery that offers significant weight, volume, and cost advantages for aerospace applications. The baseline design was successfully demonstrated through the testing of a 26-cell prototype, which completed over 7,000 44% depth-of-discharge LEO cycles at COMSAT Laboratories. Prototype designs using both nominal 5 and 10 in. diameter vessels are currently being developed for a variety of space applications.

NOTES

SMALL CAPACITY, LOW COST (Ni-H₂) DESIGN CONCEPT FOR COMMERCIAL, MILITARY, AND HIGHER-VOLUME AEROSPACE APPLICATIONS

William Cook, Ron Smith, and James Wheeler
Eagle-Picher Industries, Inc.
Joplin, Missouri 64801

Nickel-Hydrogen (Ni-H₂) batteries have become the technology of choice for both commercial and defense-related satellites in geosynchronous orbits. Their use for low-Earth-orbit (LEO) applications is not as advanced, but seems just as inevitable because of their inherent advantages over nickel-cadmium batteries. These include superior energy density, longer cycle life, and better tolerance to over-charge and reversal. Ni-H₂ cells have the added advantage in both construction and operation of not presenting the environmental possibility of cadmium pollution. Unfortunately, but necessarily, the design of these cells has been driven to high cost by the sophistication of the satellites and their uses. Now, using most of the same concepts but less costly materials and techniques, two low-cost, small cell designs have been developed. Combined with the concept of the common pressure vessel, these new designs promise to be ideal for the "small-sat" and commercial markets which, increasingly, are calling for large numbers of less-expensive satellites.

The development of Ni-H₂ cells in capacities of 20 ampere-hours (AH) or less has been delayed because of the initial demand for development of the technology for larger satellites. Two cell designs are manufactured at Eagle-Picher which are tailored to the specific requirements of the small satellite, not only in terms of power and volume, but also in terms of economic feasibility. The RNH-12-1 is a 12 AH common pressure vessel design that has been manufactured, tested, and delivered to Intraspaces Corporation for use as a power source on the SPINSAT mission. The RNH-5-1 is a new design which can be built in sizes from 5 through 120 AH in an IPV or CPV configuration. These two designs are based upon proven manufacturing processes and component heritage and therefore retain the reliability and performance advantages of their predecessors. Details of these two designs and their play in the "small sat" market will be described in this paper.

NOTES

MATHEMATICAL ANALYSES OF THE TRANSPORT AND REACTION MECHANISMS IN SOLID OXIDE FUEL CELLS

Thomas M. Maloney
Sverdrup Technology, Inc.
Lewis Research Center Group
Brookpark, Ohio 44142

and

Dennis W. Dees
Argonne National Laboratory
Argonne, Illinois

Computer models have been developed to quantitatively predict performance characteristics of high temperature H_2 - O_2 solid oxide fuel cells. Current-voltage relationships were estimated by analyzing effects due to charge transfer, surface migration, and material transport within the solid electrolyte. Model parameters included electrical conductivity, electrolyte thickness, reference exchange currents, and length of diffusion paths near the electrolyte surface. Results from the mathematical model were in close agreement with experimental data for single cells at 1000 °C and 1 atm. These results indicated that the solid electrolyte thickness should be greater than 25 μm and the average fuel cell operating current density should exceed 250 mA/cm² to maintain high current efficiencies.

NOTES

SODIUM SULFUR CELL TECHNOLOGY FLIGHT EXPERIMENT

Rebecca R. Chang
Space Systems/Loral
Palo Alto, California 94303

A practical and technically low risk sodium sulfur (Na-S) cell experiment has been identified to address all critical issues related to Na-S battery operation under microgravity conditions. This work was performed by Space Systems/Loral (SS/L) formerly known as Ford Aerospace Corporation's Space Systems Division under NASA contract NAS3-25355, Sodium Sulfur Battery Flight Experiment Definition Study (Phase A), and documented in the Phase A final report. The advantage of the Na-S battery for space applications, and the benefits, justifications, and objectives of the flight experiment were also presented at the IN-STEP 88 and previous SERT conference.

The development of a detailed experiment concept will be performed in the Concept Development Phase (Phase B); and the final design, fabrication, testing, flight, and data analysis of the experiment will be performed in the Flight Development and Operations Phase (Phase C/D). This paper summarizes the current status and update of the flight experiment.

NOTES

A REVIEW OF SODIUM - METAL CHLORIDE BATTERY ACTIVITY AT JPL

B.V. Ratnakumar, A.I. Attia, and G. Halpert
Jet Propulsion Laboratory
Pasadena, California 91109

Following the disclosures by Coetzer et al. on the use of transition metal chlorides in chloroaluminates as alternate cathodes to sulfur in rechargeable sodium batteries, several laboratories, including the Jet Propulsion Laboratory, focused their attention on these systems. These systems have certain distinct advantages over sodium-sulfur batteries such as increased safety, inherent overcharge capability, and lower operating temperatures. Two systems, i.e., Na/FeCl₂ and Na/NiCl₂, were developed extensively and evaluated in various applications including electric vehicles and space. Their performance has been very encouraging and warrants a detailed fundamental study on these cathodes.

At the Jet Propulsion Laboratory a program was initiated two years back to understand the electrochemical behavior of FeCl₂ and NiCl₂, and to identify and evaluate other transition metal chlorides of promise. The initial efforts focused on the methods of fabrication of the electrodes and their electrochemical characterization. Subsequent studies were aimed at establishing the reaction mechanism, determining the kinetics, and identifying the rate-limiting processes in the reduction of metal chloride cathodes. Nickel chloride emerged from these studies as the most promising candidate material and was taken up for further detailed study on its passivation - a rate limiting process - under different experimental conditions. Also, the feasibility of using copper chloride, which is expected to have a higher energy density, has been assessed. On the basis of the criteria established from the voltammetric response of FeCl₂, NiCl₂, and CuCl₂, several other transition metal chlorides were screened. Of these, molybdenum and cobalt appear promising.

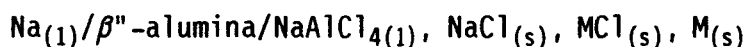
NOTES

AN AC IMPEDANCE STUDY OF THE Ni/NiCl₂ ELECTRODE OF SODIUM/METAL CHLORIDE CELLS

B.J. Dougherty, M.C.H. McKubre, S.I. Smedley, and F. Tanzella
SRI International
Menlo Park, California 94025

There is a growing interest in the use of the sodium/metal chloride cells as alternatives to sodium/sulphur cells, in many applications. Among the potential advantages of the Zebra cell over its sodium/sulphur counterpart are a lower operating temperature, easier construction, safer operation, and greater cycle life. These attributes make the sodium/metal chloride cell an excellent candidate for use in space vehicles.

The sodium/metal chloride family of cells has the general formula



where M is a transition metal such as Fe or Ni. The positive electrode consists of a solid, porous metal matrix, which is usually constructed in the fully discharged state by co-sintering metal powder and NaCl powder, and then impregnating the product with molten NaAlCl₄. The porosity and morphology of the electrode play a key role in determining the energy density of these batteries.

We have used ac impedance spectroscopy to elucidate the reaction mechanism of the Ni/NiCl₂ electrode, and to examine the influence of the electrode porosity and morphology on the operation of this electrode. As a result, we have developed a novel cell design and electrode construction technique.

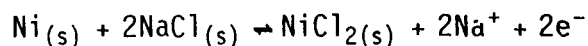
The electrodes are constructed in the half-charged state by mixing together the appropriate ratio of Ni, NaCl, NiCl₂, and NaAlCl₄ powders. In general, this ratio is chosen so as to produce an electrode in which 30% of the metal is converted to the metal chloride when the cell is fully charged. With the exception of NaAlCl₄, all powder samples are dried at 110 °C prior to electrode construction. The NaAlCl₄ is used as received. The preparation of the electrode mixture is carried out inside an argon-filled glove box. Once the powders have been mixed, they are packed directly into the electrode chambers of the electrochemical cell, which is then sealed and transferred from the glove box to a furnace at 250 °C.

The electrochemical cell used in this study contains two back-to-back Ni/NiCl₂ electrodes, separated by a disc of β'' -alumina. Under an applied current or voltage, one electrode is discharged while the other is charged. The impedances of both half-cells and the whole cell are measured simultaneously, using a four-channeled Solartron 1254 FRA, as a function of the state of discharge of the cell and cycle number. This approach enables us to deduce the mechanisms of both the charge and discharge reactions, and to follow changes in the effective resistance of the β'' -alumina.

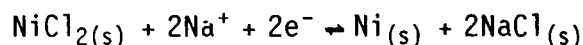
The impedance spectra of the whole cell display three features: two capacitive loops at frequencies greater than 1 Hz and a diffusion-related relaxation at lower frequencies. The frequency dependence of the impedance is

typical of systems in which the electrochemical reactions take place throughout a 3-D porous electrode matrix and suggests that an electrical transmission line model may be an appropriate choice to describe this system.

In the half-cell being charged, the overall reaction can be written



Here, the magnitude of the impedance increases slowly with the state of charge, which may be due to the formation of NiCl_2 on the active surface of the electrode. Conversely, the impedance of the discharging half cell, in which the reverse reaction



occurs, displays the opposite trends.

Once we have a better understanding of the mechanism of the Ni/NiCl_2 electrode, and of the way in which this is influenced by factors such as electrode porosity and morphology, we intend to extend this study to other metal/metal chloride electrodes in this family of cells.

ADVANCES IN Li-TiS₂ CELL TECHNOLOGY

S. Surampudi, D.H. Shen, C.-K. Huang, F. Deligiannis,
A.I. Attia, and G. Halpert
Jet Propulsion Laboratory
Pasadena, California 91109

JPL is involved in a NASA sponsored program to develop ambient temperature secondary Lithium - Titanium Disulfide Cells for future space missions. After several years of research on various lithium systems, the Li-TiS₂ system was selected for development in view of its practically realizable high specific energy. In the last two years, the efforts were focused on improving the cycle life of the system and optimizing the cell design. A number of approaches, such as the use of mixed solvent electrolytes, the use of alternate anode materials, the operation of cells at low temperature, and the cycling of cells under optimized voltage limits, are examined to improve the cycle life performance of this system. Cycling studies in small 150 mAh cells have identified 1.5 M LiAsF₆/2-MeTHF, 1.5 M LiAsF₆/EC+2-MeTHF, and 1.5 M LiAsF₆/THF+2-MeTHF+2-MeF as promising electrolytes for Li-TiS₂ cells. Li-Al and Li-C were selected for further assessment as candidate anode materials after a detailed theoretical and experimental evaluation. Cycling of the cells at low temperature did not result in improving the cycle life of the cells. Charge and discharge voltage limits were found to have significant influence on the cycle life of the cells activated with 1.5 M LiAsF₆/THF+2-MeTHF+2-MeF electrolyte. The influence of design variables, such as ratio of electrode capacity, quantity of electrolyte, pack tightness, cell configuration, etc., on the cycle life performance are being examined as a part of the design optimization study. Spiral-wound 1 Ah cells fabricated for the design studies have completed more than 500 cycles at 50% DOD. This paper summarizes the advances made in the Li-TiS₂ technology at JPL since 1989.

NOTES

LITHIUM POLYMER BATTERIES

Boone B. Owens
University of Minnesota
Minneapolis, Minnesota 55455

Lithium batteries offer many advantages including high specific energy, high output cell voltages, very low self-discharge rates and, in some cases, the ability to operate at low or high extremes of temperature. Ambient temperature rechargeable lithium batteries have been an active research area during the past fifteen years. These batteries may be categorized as

- (1) Liquid depolarizer batteries that use (electroactive) inorganic liquids as the electrolyte
- (2) Polymer cathode batteries that use organic liquid electrolytes combined with solid polymer redox cathodes
- (3) Solid cathode batteries that use organic liquid electrolytes with solid insertion cathodes
- (4) Polymer electrolyte batteries that use solid polymer electrolytes with solid insertion (intercalation) cathodes

Rechargeable coin cells (with Li alloy anodes) are available from several manufacturers, and larger cells will become available as the technology evolves.

A unique class of rechargeable lithium batteries is the "polymer electrolyte" group. This group is similar to the above indicated "solid cathode" class, except that the electrolyte is a solid high molecular weight material instead of a liquid low molecular weight organic compound (or mixture). Two significant properties result from this. First, the solid electrolyte has a much lower vapor pressure and in principle, during times of abuse, will be safer with respect to volatilization, explosion, and ignition. Second, because the electrolyte is a solid polymeric material, it can be fabricated in the form of a thin film and no other separator element is required. As a result, the very thin electrolyte, combined with thin electrode structures, allows superior high rate performance and improved lithium plating morphology.

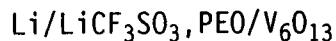
Lithium polymer electrolyte batteries have been under development by several groups for approximately ten years. Advantages of these batteries include

Stable Electrolyte Materials
Low Electrode Loading
Wide Electrochemical Window
Flexible Shape Factor

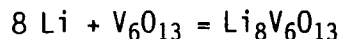
Non-volatile, Solid State
Better Li Cyclability
High Energy Cathodes
Efficient Packaging

These batteries are based upon a unique battery design that incorporates very large area electrolyte and electrode layers of 10-100 μm thickness, such that the ohmic losses associated with the impedance of the electrolyte are minimized and the electrode kinetics are enhanced. The attractiveness of this system resides in its all solid state nature and the apparent ability to harness the energy of lithium in a rechargeable cell design that may permit relatively high deliverable energies and power levels. This solid state

design has worked surprisingly well in tests on very small cells where high energy efficiencies and several hundred cycles have been reported for a cell operating at about 100 °C. A typical cell is



for which the cell reaction is



Modeling studies suggest that energy density values of 100-300 Wh/Kg or 150-450 Wh/L and power density values of 100-1000 W/kg or 150-1500 W/L may be achieved.

The aspect of greater intrinsic safety combined with improved rate capability makes the polymer electrolyte battery system a candidate for high reliability applications. Problem areas that need further investigation include capacity fading, cyclic life, materials degradation, cost, multicell designs, cell balance, overcharge, overdischarge, rate capability, thermal management, and safety.



National Aeronautics and
Space Administration

Report Documentation Page

1. Report No. NASA CP - 10067		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle Space Electrochemical Research and Technology Abstracts				5. Report Date	
				6. Performing Organization Code	
7. Author(s)				8. Performing Organization Report No. E - 6089	
				10. Work Unit No. 506 - 41 - 21	
9. Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135 - 3191				11. Contract or Grant No.	
				13. Type of Report and Period Covered Conference Publication	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546 - 0001				14. Sponsoring Agency Code	
15. Supplementary Notes Conference agenda and abstracts only.					
16. Abstract <p>This document contains abstracts of the proceedings of NASA's third Space Electrochemical Research and Technology (SERT) Conference, held at the NASA Lewis Research Center on April 9-10, 1991. The objective of the conference was to assess the present status and general thrust of research and development in those areas of electrochemical technology required to enable NASA missions into the next century. The conference provided a forum for the exchange of ideas and opinions of those actively involved in the field, in order to define new opportunities for the application of electrochemical processes in future NASA missions. Papers were presented in three technical areas: the electrochemical interface, the next generation in aerospace batteries and fuel cells, and electrochemistry for non-energy storage applications. This document contains the abstracts of the papers presented.</p>					
17. Key Words (Suggested by Author(s)) Electrochemistry Batteries Fuel cells			18. Distribution Statement Unclassified - Unlimited Subject Category 44		
19. Security Classif. (of the report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of pages 65	22. Price* A04